

Accurate ab initio calculations which demonstrate a
 $^3\Pi_u$ ground state for Al_2

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Abstract

The spectroscopic parameters and separations between the three low-lying $X^3\Pi_u$, $A^3\Sigma_g^-$ and $a^1\Sigma_g^+$ states of Al_2 are studied as a function of both the one-particle and n-particle basis sets. Approximate correlation treatments are calibrated against full CI calculations correlating the six valence electrons in a double-zeta plus two d-function basis set. Since the CASSCF/MRCI $^3\Pi_u - ^3\Sigma_g^-$ separation is in excellent agreement with the FCI value, the MRCI calculations were carried out in an extended $(20s13p6d4f)/[6s5p3d2f]$ gaussian basis. Including a small correction for relativistic effects, our best estimate is that the $^3\Sigma_g^-$ state lies 174 cm^{-1} above the $^3\Pi_u$ ground state. The $^1\Sigma_g^+$ state lies at least 2000 cm^{-1} higher in energy. At the CPF level, inclusion of 2s and 2p correlation has little effect on D_e , reduces T_e by only 26 cm^{-1} , and shortens the bond lengths by about 0.02 a_0 . Further strong support for a $^3\Pi_u$ ground state comes from the experimental absorption spectra, since both observed transitions can be convincingly assigned as $^3\Pi_u \rightarrow ^3\Pi_g$. The $(2)^3\Pi_g$ state is observed to be sensitive to the level of correlation treatment, and to have its minimum shifted to shorter r values, such that the strongest experimental absorption peak probably corresponds to the $0 \rightarrow 2$ transition.

(NASA-TM-89302) ACCURATE AB INITIO
 CALCULATIONS WHICH DEMONSTRATE A $^3\Pi_u$
 GROUND STATE FOR Al_2 (NASA) 22 p Avail:
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I. Introduction

The three potential candidates for the ground state of Al_2 arise from the $^2P(3s^23p^1)$ ground state of Al atom. The $^1\Sigma_g^+$ ($5\sigma_g^2$) state involves the formation of a two-electron σ bond, the $^3\Pi_u$ ($5\sigma_g^1 2\pi_u^1$) state involves the formation of a one-electron σ bond and a one-electron π bond, and the $^3\Sigma_g^-$ ($2\pi_u^2$) state involves the formation of two one-electron π bonds. All three of these states have been proposed as the ground state.

The double-headed, red-degraded band observed in emission in the wave length region between 5650-6600 Å was assigned by Ginter et al. [1] as either a $^3\Sigma_u^- - ^3\Sigma_g^-$ or $^3\Sigma_u^+ - ^3\Sigma_g^+$ transition. Since $^3\Sigma_g^-$ is one of the possible ground states, and the excitation $5\sigma_g \rightarrow 5\sigma_u$ yields an excited state of the correct symmetry, they suggested that the ground state is $^3\Sigma_g^-$. Recent calculations of Upton [2] support this assignment, but the theoretical calculation that placed the $^3\Sigma_g^-$ state 486 cm^{-1} lower than $^3\Pi_u$ was not considered to be definitive.

Better information concerning the identification of the ground state can be derived from the absorption spectra of the group IIIA metal dimers. Douglas et al. [3] observed two band systems for Al_2 in krypton matrices at 15K, one with a broad peak (1800 cm^{-1} fwhm) at $14\,300 \text{ cm}^{-1}$, and one with four peaks in the range $24\,493$ to $25\,227 \text{ cm}^{-1}$. The band systems are different from the band observed in emission. Based upon a qualitative argument that the ground state of In_2 is $^1\Sigma_g^+$, and analogies with Ga_2 and In_2 spectra where similar transitions are observed, they assigned the ground state of Al_2 as $^1\Sigma_g^+$. Abe and Kolb [4] have also recorded the absorption spectrum of Al_2 in Ar, Kr and Xe matrices. Like Douglas et al. [3], they observe a band near $25\,000 \text{ cm}^{-1}$. The vibrational frequency of the upper state was given as $238 \pm 5 \text{ cm}^{-1}$, which is in reasonable accord with the average ΔG_v of 245 cm^{-1} reported by Douglas et al. [3]. Abe and Kolb [4] also did not observe the band seen in emission.

Basch et al. [5] have predicted a $^3\Pi_u$ ground state based upon ab initio calculations. The calculated $^3\Pi_u - ^3\Sigma_g^-$ splitting of 324 cm^{-1} was considered to be too small for a definitive prediction of the ground state. By considering the low-lying excited states, they were able to show that the absorption spectra were much more consistent with a $^3\Pi_u$ ground state. They assigned the broad peak centered at

14 300 cm^{-1} to a transition to a repulsive $(1)^3\Pi_g$ state. The upper state of the band centered near 25 000 cm^{-1} was assigned as $(2)^3\Pi_g$. While the upper state was computed to lie at the correct excitation energy, their computed vibrational frequency of 129 cm^{-1} is almost a factor of two different from that determined by Douglas et al. [3] or Abe and Kolb [4], a difference much larger than their errors for the experimentally characterized bound states.

In this work we also consider the question of the ground state of Al_2 . We determine the computational requirements for accurately describing the spectroscopic constants (r_e , ω_e , D_e and T_e) for all three candidates for the ground state. Previous theoretical work [2,5] obtained r_e values that were considerably larger than experiment [1,6]. Full CI (FCI) calculations are used to calibrate our approximate methods of including electron correlation. CASSCF/MRCI calculations, which accurately reproduce the FCI results in the valence DZ + 2d gaussian basis, are carried to chemical accuracy by the use of extensive one-particle basis sets. In addition to valence 3s and 3p correlation, we consider the effect of 2s and 2p correlation and relativistic effects. Our spectroscopic parameters are in excellent agreement with the available experimental data. Sufficient accuracy in T_e is achieved that although the calculations place the $^3\Sigma_g^-$ state less than 200 cm^{-1} above, the calculations provide strong support for a $^3\Pi_u$ ground state. In addition, we also consider several excited states. The uncertainty in the Basch et al. [5] assignment of the spectrum of Douglas et al. [3] is eliminated by showing that the computed vibrational frequency of the $(2)^3\Pi_g$ state and the Franck-Condon factors for the $(1)^3\Pi_u - (2)^3\Pi_g$ transition are consistent with the spectrum obtained by Douglas et al. [3] and Abe and Kolb [4]. It is therefore concluded that the ground state is $^3\Pi_u$.

II. Methods

A full configuration-interaction (FCI) expansion grows rapidly with the size of the one-particle basis, making it essential to use a compact basis to provide the best possible benchmark calculation. This is achieved for Al by using a general contraction based upon atomic natural orbitals (ANO). Recently, Almlöf and Taylor [7] have shown that such contractions yield a small loss in accuracy in molecular calculations, both at the SCF and correlated levels. Our first series of basis sets are

based upon the 12s9p primitive set of Huzinaga [8] as tabulated by McLean and Chandler [9] with three d functions added ($\alpha_d=0.5,0.2,0.08$). The ANO basis sets are contracted to [4s3p1d], [4s3p2d], [5s4p1d] and [5s4p2d] based on a three-electron correlation treatment of the atom. These basis sets are used in the FCI benchmark calculations and for the study of the excited states of Al_2 .

In addition, to study the convergence of the spectroscopic parameters and excitation energies with extension of the one-particle basis set, three distinctly different large basis sets are used to avoid an inequivalent treatment of the three low-lying states. One of the large sets is constructed using the ANO procedure based on a 20s13p even-tempered valence set taken from Schmidt and Ruedenberg [10]. This is augmented with an even-tempered (6d4f) polarization set with exponents chosen as $\alpha=2.5^n\alpha_o$, where $n=0,k$ and with $\alpha_o(d)=0.03$ and $\alpha_o(f)=0.10$. The mean of the exponent range was based on the work of Ahlrichs and Taylor [11]. The factor of 2.5 is typical for large saturated basis sets. This basis set is then contracted as (20s13p6d4f)/[6s5p3d2f] based upon atomic calculations correlating only the 3s and 3p electrons. Hence this basis, denoted BIG-ANO, is used only to correlate the 3s and 3p electrons.

The second large GTO basis set is derived from the work of McLean and Chandler [9], which has a triple-zeta description of the 2p and 3p orbitals, and a double-zeta description of the 2s and 3s orbitals. This basis set was improved by splitting the outer four s functions into seven functions. The inner s and p functions are contracted following McLean and Chandler [9]. Five 3d and three 4f functions are added. The polarization basis contains tight functions and the contraction of the valence basis set is sufficiently flexible to allow correlation of the 2s and 2p electrons as well as the 3s and 3p. This basis set is given in Table I and is denoted as BIG-GTO. For this, and all other GTO basis sets, the 3s component of the 3d function and the 4p component of the 4f functions have been deleted.

The final large basis set is an 8s7p4d2f STO basis set which is given in Table II. This set is developed from the 7s3p Al^+ basis set of Clementi and Roetti [12]. This is augmented with four 3p functions to describe the 3p orbital and with four 3d and two 4f functions. The 3d exponents are taken from Ref. 13. The polarization basis is not sufficiently compact to correlate the 2s and 2p electrons, but this basis set, as

well as the two large GTO bases, should be very close to the 3s and 3p correlation limit.

Electron correlation is included using both single-reference treatments based on SCF orbitals, and multi-reference treatments based upon complete-active space self-consistent field (CASSCF) [14] orbitals with the 3s and 3p orbitals and electrons as active. The importance of higher than double excitations in the single-reference treatments is estimated using both the Davidson correction (+Q) [15] and the coupled-pair functional (CPF) approach [16]. The MRCI treatments include both second-order CI (SOCi), i.e. single and double excitations from all configurations in the CASSCF wave function, as well as selected reference treatments. The reference includes all occupations that have CSFs with coefficients greater than 0.05 in the CASSCF wave function near r_e . For the ${}^3\Sigma_g^-$ state there are 12 reference occupations resulting in 30 CSFs, while for the ${}^3\Pi_u$ state there are 10 reference occupation or 22 CSFs. In both the SOCi and MRCI calculations, the importance of higher excitations is estimated using the multi-reference analog [17] of the Davidson correction. In most correlated calculations only six electrons (the 3s and 3p) are correlated, however in some SDCl and CPF calculations the 2s and 2p electrons are correlated as well. These 22 electron treatments are denoted as SDCl(22) and CPF(22).

In calculations on the second state of ${}^3\Pi_g$ symmetry, it was necessary to optimize the orbitals for the average of the (1) ${}^3\Pi_g$ and (2) ${}^3\Pi_g$ states to avoid CASSCF convergence difficulties encountered at some bond lengths. At bond distances where it was possible to optimize the orbitals for the second root, it is found that averaging for two roots degrades the CASSCF description of the second root by about 0.2 eV. However at the SOCi level, the difference between using orbitals determined from optimizing for the second root or the average orbitals is less than 0.01 eV. Since optimizing the orbitals for the average of the two roots does not significantly degrade the SOCi description, average CASSCF orbitals were used to determine the (2) ${}^3\Pi_g$ state potential.

The dissociation energies, D_e , reported here are computed using a supermolecule approach. For the SDCl and CPF wave functions, the ${}^3\Sigma_u^+$ state with occupation $3p\sigma_g^1 3p\sigma_u^1$ with a bond length of 100 a_0 is used for infinite separation.

Since the CASSCF wave functions correctly dissociate to neutral atoms, the SOCI D_e is computed using the energy of the $^3\Sigma_g^-$ state with an Al-Al separation of $100 a_0$. The spectroscopic parameters (r_e and ω_e) for the $^3\Pi_u$, $^3\Sigma_g^-$ and $^1\Sigma_g^+$ states are determined by a fit in $1/r$. The Franck-Condon factors for the $X^3\Pi_u \rightarrow 2^3\Pi_g$ transition are computed using the ab initio potentials from vibrational wave functions determined using a finite difference approach.

The Darwin and mass-velocity relativistic effects [18] are incorporated using first-order perturbation theory. Previous work [19] has shown that the relativistic effects estimated in this way are similar to that computed for an optimized wave function. The FCI calculations have been performed using a modified version of the Knowles and Handy FCI program [20,21] which has been interfaced to the MOLECULE-SWEDEN [22,23] codes. All FCI calculations were performed on the NAS CRAY 2.

III. Results and discussion

The spectroscopic parameters at various levels of treatment for the $X^3\Pi_u$, $A^3\Sigma_g^-$, and $a^1\Sigma_g^+$ states of Al_2 are summarized in Tables III-V, respectively. We first calibrate different approaches for truncating the n -particle space in the $[4s3p1d]$ basis set. Compared to the FCI, the SDCI r_e is 0.01 - $0.02 a_0$ too short, D_e for the $^3\Pi$ state is 0.125 eV too small, and T_e for the $^3\Sigma_g^-$ state is over 800 cm^{-1} too large. Although these errors are reduced at the CPF level, they are still too large for a quantitative estimate of D_e and especially T_e . Thus while the single-reference treatments are sufficiently accurate to study the effect of basis set saturation, only the SOCI gives a reliable prediction of the ground state. Note that in both the $[4s3p1d]$ and $[4s3p2d]$ bases, the SOCI spectroscopic parameters and T_e are in significantly better agreement with the FCI before a correction is applied for higher excitations ($+Q$). The selection of reference occupations results in a T_e which is too small, but in many applications reducing the number of reference CSFs while degrading T_e by only 100 cm^{-1} is quite acceptable. For the MRCI calculations with selected references, the inclusion of the Davidson correction also causes an overshoot of the FCI r_e and T_e .

Since the addition of a second d function has a larger effect on the $^3\Pi_u$ - $^3\Sigma_g^-$

separation than does expanding the valence space to [5s4p], a second set of FCI calibration calculations is performed using the [4s3p2d] basis set. Since r_e and ω_e are not greatly affected by the level of correlation treatment, the calibration calculations are performed near the SDCI minimum, and only T_e and D_e are determined. In the [4s3p2d] basis set, the FCI $^3\Pi_u - ^3\Sigma_g^-$ separation is 130 cm^{-1} smaller and the D_e is 0.027 eV larger than in the [4s3p1d] basis. The improvement in the d basis results in a small decrease in T_e and increase in D_e at all levels of correlation treatment, but as for the [4s3p1d] basis set results, only the SOCI is in excellent agreement with the FCI.

Since the FCI calibration calculations show that the SOCI treatment accounts for essentially all of the valence correlation effect on T_e , and relativistic effects and differential 2s and 2p correlation effects are small (see below), the SOCI should converge to the true value in the limit of a complete one-particle basis. We therefore consider the $^3\Pi_u - ^3\Sigma_g^-$ separation in three larger basis sets. In the STO and two large gaussian basis sets, the SDCI and CPF T_e differ by only 42 cm^{-1} . The CPF D_e values for the $^3\Pi_u$ state agree well for the two GTO basis sets, but are about 0.1 eV less than the SOCI+Q value, which should be near the FCI value in this basis. The r_e obtained in the larger basis sets is within $0.04\text{--}0.05\text{ }a_0$ of the experimental value for the $^3\Sigma_g^-$ state. At least half of this remaining difference is likely due to 2s and 2p correlation. The fact that a slightly larger r_e value is obtained using the BIG-ANO basis set may be due to a smaller superposition error because the contraction is based on a correlated treatment of the atoms. However, in spite of a potential bias towards the separated atoms, the BIG-ANO basis set has a slightly larger D_e than the BIG-GTO basis set. The BIG-ANO basis set also recovers the largest correlation energy for the $^3\Pi_u$ state at a bond length of $5.1\text{ }a_0$. (Note that the correlation energies vary by only 0.03 eV between basis sets out of a total SDCI valence correlation energy of 3.24 eV .) Hence, the SOCI treatment in the BIG-ANO basis is expected to be our most accurate calculation. The resulting T_e value of 165 cm^{-1} is expected to be very close to the FCI value for this large basis set. Note that the MRCI T_e value is 88 cm^{-1} smaller than the SOCI value in the BIG-ANO basis, which is very similar to the 77 cm^{-1} difference found for the [4s3p1d] basis set. Although this is a very small error, it is on the order of half our best estimate

for the separation.

The inclusion of relativistic effects using first-order perturbation theory increases the SOCI T_e value by only 9 cm^{-1} in the BIG-ANO basis. Also, including the 2s and 2p electrons in the correlation treatment increases T_e by 26 cm^{-1} at the CPF level in the BIG-GTO basis. Hence, the differential 2s and 2p correlation effect is the same size, but opposite in direction to the difference between the FCI and SOCI T_e in the smaller basis sets. The fact that 2s and 2p correlation increases the SDCI T_e by more than 400 cm^{-1} is attributed to the larger size consistency error, which also manifests itself as a decrease in the D_e . Hence, neither relativistic effects nor 2s and 2p correlation are likely to change our prediction of a $^3\Pi_u$ ground state.

Our best estimate for the $X^3\Pi_u-A^3\Sigma_g^-$ separation of 174 cm^{-1} is slightly smaller than the value of 324 cm^{-1} reported by Basch et al. [5]. This difference can easily be attributed to the smaller basis set and first-order CI treatment employed in the earlier theoretical study. On the other hand, Upton [2] found the $^3\Sigma_g^-$ to be lower by 486 cm^{-1} . An SCF/SDCI treatment in a $(10s6s1d)/[6s4p1d]$ basis (with the same d exponent as used by Upton) yields a $^3\Pi_u$ ground state, but the CASSCF treatment in all of our basis sets incorrectly places the $^3\Sigma_g^-$ state below the $^3\Pi_u$. For example, in the $[5s4p2d]$ basis set the $^3\Sigma_g^-$ state is 934 cm^{-1} below the $^3\Pi_u$, but 160 cm^{-1} above it in the SOCI calculation. Therefore, it was probably the level of correlation treatment rather than the basis set that led to the incorrect ground state in the earlier theoretical study of Upton [2].

Our best value for D_0 of 1.4 eV is within the error bounds of the experimental value of $1.55\pm0.15\text{ eV}$ determined by Stearns and Kohl [24] using a Knudsen cell mass spectrometric method and assuming a $^3\Sigma_g^-$ ground state. Our calculations support this value, which is recommended by Huber and Herzberg [6], in preference to the $1.78\pm0.19\text{ eV}$ value reported by Uy and Drowart [25], also determined using a Knudsen cell mass spectrometer. Some revision of the experimental values may occur if evaluated with a partition function that correctly accounts for both triplet states.

Previous theoretical work obtained bond lengths for the $^3\Sigma_g^-$ state that were up to $0.16 a_0$ too long [5]. The FCI calculations show that the bond length is much

more sensitive to the one-particle basis than to the level of correlation treatment when the six valence electrons are correlated. For the [5s4p2d] basis set, even the CASSCF value is only $0.031 a_0$ longer than the SOCI value, which is $0.086 a_0$ longer than experiment. This is similar to the error reported by Upton [2], and about half that of Basch et al. [5]. Given the consistency of our small basis set values and the similarity of the Upton value, it seems likely that the use of an effective-core potential contributed to the error in the Basch et al. [5] r_e value. Expanding the basis set reduces the error in r_e by about half, and the inclusion of 2s and 2p correlation also shortens the bond length, while the inclusion of relativity has little effect. Our best value is within $0.02 a_0$ of the experimental value for the $^3\Sigma_g^-$ state. Hence, to achieve accurate r_e values for Al_2 requires a very extensive basis set as well as inclusion of 2s and 2p correlation. Since the trends in r_e with basis set improvement and correlation treatment are similar for the $^3\Pi_u$ and $^3\Sigma_g^-$ states, we estimate $5.08 \pm 0.02 a_0$ for the $^3\Pi_u$ state r_e .

Our theoretical spectroscopic parameters for the $a^1\Sigma_g^+$ state are summarized in Table V. Douglas et al. [3] suggested that this was the ground state on the basis of analogy with the absorption spectra of Ga_2 and In_2 . The FCI calibration calculations show that CPF produces equivalent results for the $^3\Pi_u$ and $^1\Sigma_g^+$ states. Therefore, the CPF treatment in conjunction with an extended one-particle basis set should give a reliable estimate of T_e . As for the $^3\Pi_u - ^3\Sigma_g^-$ separation, the BIG-GTO and STO basis sets yield very similar separations. The inclusion of 2s and 2p correlation increases the separation slightly at the CPF level. The theoretical calculations confirm that the $a^1\Sigma_g^+$ lies at least 2000 cm^{-1} above the $X^3\Pi_u$ ground state.

While the theoretical calculations by themselves are convincing support for a $^3\Pi_u$ ground state, further confirmation comes from the assignment of the experimental absorption spectra. Basch et al. [5] have assigned the two peaks observed in absorption to $^3\Pi_u \rightarrow ^3\Pi_g$ transitions. The only problem with this assignment is that their computed vibrational frequency for the $(2)^3\Pi_g$ state is about half the value deduced from the absorption spectra. In the remainder of this work we present calculations on the $(2)^3\Pi_g$ state that demonstrate that it is consistent with the upper state observed in the absorption spectra near $25\,000 \text{ cm}^{-1}$. These cal-

culations employ the [5s4p2d] gaussian basis that gave spectroscopic parameters in good agreement with the larger BIG-ANO basis.

For the $(2)^3\Pi_g$ state we obtain a double well potential at the CASSCF level, with the outer well characterized by the parameters $r_e=5.57 a_0$ and $\omega_e=291 \text{ cm}^{-1}$. When additional correlation is added through a SOCI, ω_e for this outer well decreases to 131 cm^{-1} in good agreement with the value reported by Basch et al. [5], but a second, deeper, minimum occurs at shorter r . At the SOCI level there is a small barrier between the two wells which is eliminated with the inclusion of the Davidson correction. The r_e of this state is computed to be $4.577(4.591) a_0$ at the SOCI(SOCI+Q) levels. At $5.5 a_0$ the $(2)^3\Pi_g$ state is dominated by the occupations

$$3s\sigma_g^2 3p\sigma_g^2 3s\sigma_u^1 3\pi_u^1, \quad (1)$$

$$3s\sigma_g^2 3s\sigma_u^1 3\pi_u^3, \quad (2)$$

and

$$3s\sigma_g^2 3s\sigma_u^2 3p\sigma_u^1 3\pi_u^1, \quad (3)$$

while at $4.5 a_0$ it is dominated by (1), (2) and

$$3s\sigma_g^2 3p\sigma_g^1 3s\sigma_u^2 3\pi_g^1. \quad (4)$$

Since occupations 1, 3, and 4 are all single excitations away from the dominant configuration of the $^3\Pi_u$ state, a strong transition moment is expected, and this is qualitatively confirmed by computing non-orthogonal transition moments from the CASSCF wave functions.

Since the $(2)^3\Pi_g$ state is effectively a double well potential, or at least a superposition of two differently shaped potentials, ω_e yields little information about the shape of the potential. Therefore, we report ΔG_v values for the $(2)^3\Pi_g$ state in Table VI along with the Franck-Condon factors for the $^3\Pi_u-(2)^3\Pi_g$ transition. The vibrational wave functions were based on the SOCI+Q potentials. The $0 \rightarrow 0$ transition is weak and is probably not observed by Douglas et al. [3], but is the first transition observed by Abe and Kolb [4]. The stronger $0 \rightarrow 1$ transition probably corresponds to the first peak observed by Douglas et al. at 24493 cm^{-1} . The computed value of 23755 cm^{-1} is in reasonable accord. If we make this assignment, the

upper state experimental ΔG_v values of 263, 240, and 231 cm^{-1} should correspond to the computed values of 212, 154, and 136 cm^{-1} . The agreement is not as good as for ω_e for the $^3\Sigma_g^-$ state, because the shape of the $(2)^3\Pi_g$ potential is very sensitive to the level of correlation treatment, changing from a double-well potential into an unusual single-well potential. The $0 \rightarrow 2$ transition is found to be the strongest, while the $0 \rightarrow 3$ and $0 \rightarrow 1$ transitions have comparable strength. If we use the SOCI potential instead of the SOCI+Q potential, the $0 \rightarrow 2$ transition is still by far the strongest, but $0 \rightarrow 3$ is significantly stronger than $0 \rightarrow 1$, which is more consistent with the spectra of Abe and Kolb [4]. However the upper state ΔG_v values computed using the SOCI potential are in significantly poorer agreement with experiment. The errors in the upper state are far larger than in the three lower states, since the shape of the curve is very dependent upon the level of correlation treatment. However, overall the Franck-Condon factors and differences in the vibrational levels support assigning the absorption spectra to a $^3\Pi_u - (2)^3\Pi_g$ transition, thereby corroborating a $^3\Pi_u$ ground state. Since the Basch et al. [5] potential contained only the outer well, their computed ω_e did not correspond well with the average ΔG_v values deduced from experiment. However, they did correctly assign the transitions recorded in the absorption spectra. Our improved potential for the $(2)^3\Pi_g$ state leaves no doubt that the ground state of Al_2 is $^3\Pi_u$.

V. Conclusions.

Full CI calculation are used to calibrate other correlation methods for the accurate calculation of the low-lying states in Al_2 . Since the CASSCF/SOCI treatment is in excellent agreement with the FCI results, this treatment is carried out in an extended one-particle basis set. In this basis set, the SOCI calculations yield a $^3\Pi_u$ ground state by 165 cm^{-1} . The inclusion of relativistic effects increases the separation between the two lowest states by 9 cm^{-1} . Inclusion of 2s and 2p correlation at the CPF level changes the $^3\Pi_u - ^3\Sigma_g^-$ separation by less than the difference between the FCI and SOCI calculations in the smaller basis sets. This leads to the prediction of a 174 cm^{-1} separation between the ground $^3\Pi_u$ state and the $^3\Sigma_g^-$ state. The ground state identity is confirmed by showing that the experimental absorption spectra arises from transitions from the $^3\Pi_u$ ground state to the first two states of

$^3\Pi_g$ symmetry as suggested by Basch et al. [5]. Our computed D_0 supports the lower experimental value [24] of 1.55 ± 0.15 eV, but suggests that the correct value is in the lower half of the experimental range. It is shown that the bond length of Al_2 is very sensitive to the basis set, but not to the level of correlation treatment. Using an extended gaussian basis and including 2s and 2p correlation results in an r_e for the $^3\Sigma_g^-$ state that is in good agreement with experiment.

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Table I. Orbital exponents and coefficients for the BIG-GTO gaussian basis.

function-term	exponent	coeff	function-term	exponent	coeff
s			p		
1-1	54866.49000	0.000839	1-1	259.2840	0.009448
1-2	8211.77000	0.006527	1-2	61.0769	0.070974
1-3	1866.18000	0.033666	1-3	19.3032	0.295636
1-4	531.12900	0.132902	1-4	7.0109	0.728219
1-5	175.11800	0.401266	2-1	2.6739	1.000000
1-6	64.00550	0.531338	3-1	1.0366	1.000000
2-1	64.00550	0.202305	4-1	0.3168	1.000000
2-2	25.29250	0.624790	5-1	0.1143	1.000000
2-3	10.53490	0.227439	6-1	0.0414	1.000000
3-1	4.35930	1.000000	d		
4-1	2.17965	1.000000	1-1	9.00	1.000000
5-1	1.08980	1.000000	2-1	3.00	1.000000
6-1	0.50000	1.000000	3-1	1.00	1.000000
7-1	0.21470	1.000000	4-1	0.30	1.000000
8-1	0.10730	1.000000	5-1	0.10	1.000000
9-1	0.05370	1.000000	f		
1-1	1.305	1.000000			
2-1	0.446	1.000000			
3-1	0.100	1.000000			

Table II. Orbital exponents for the Al STO basis set.

1s	20.82510	2p	10.42940	3d	4.00
1s	13.41920	2p	5.69821	3d	2.80
2s	12.17030	2p	3.28098	3d	1.60
2s	4.83620	3p	2.90000	3d	0.95
3s	3.88799	3p	1.77513		
3s	1.77513	3p	1.25381	4f	3.60
3s	1.25381	3p	0.88600	4f	1.80
3s	0.88600				

Table III. Comparison of $\text{Al}_2 \text{X}^3\Pi_u$ spectroscopic constants with level of basis set and correlation treatment.

	$r_e (a_o)$	$\omega_e (\text{cm}^{-1})$	$D_e(\text{eV})$
SDCI[4s3p1d]	5.224	274	1.081
CPF[4s3p1d]	5.234	267	1.119
MRCI[4s3p1d]	5.233	267	...
MRCI+Q[4s3p1d]	5.242	264	...
SOCI+Q[4s3p1d]	5.244	264	1.208
FCI[4s3p1d]	5.240	265	1.206
SDCI[5s4p1d]	5.209	273	1.103
CPF[5s4p1d]	5.220	270	1.160
SDCI[4s3p2d]	5.204	269	1.103
CPF[4s3p2d]	5.212	265	1.159
SOCI[4s3p2d]	1.231 ^a
SOCI+Q[4s3p2d]	1.235 ^a
FCI[4s3p2d]	1.233 ^a
SDCI[5s4p2d]	5.189	268	1.124
CPF[5s4p2d]	5.198	264	1.181
SOCI[5s4p2d]	5.202	263	1.261
SOCI+Q[5s4p2d]	5.204	261	1.242
SDCI BIG-GTO	5.131	285	1.240
CPF BIG-GTO	5.133	283	1.311
SDCI BIG-GTO(22)	5.104	286	1.153
CPF BIG-GTO(22)	5.113	281	1.309
SDCI STO	5.129	287	...
CPF STO	5.130	285	...
SDCI BIG-ANO	5.145	281	1.248
CPF BIG-ANO	5.148	277	1.320
MRCI BIG-ANO	5.233	282	...
MRCI+Q BIG-ANO	5.231	280	...
SOCI BIG-ANO	5.153	277	1.401
SOCI+Q BIG-ANO	5.151	277	1.425
SOCI+Rel ^b BIG-ANO	5.154	277	1.386
EXPT			1.55±0.15

^a The bond length is 5.200.

^b Indicates that an estimate of relativistic effects was included.

Table IV. Comparison of $\text{Al}_2 \text{ A}^3\Sigma_g^-$ spectroscopic constants with level of basis set and correlation treatment.

	$r_e (a_o)$	$\omega_e (\text{cm}^{-1})$	$T_e(\text{cm}^{-1})$
SDCI[4s3p1d]	4.781	327	1107
CPF[4s3p1d]	4.792	324	802
MRCI[4s3p1d]	4.785	327	175
MRCI+Q[4s3p1d]	4.795	324	488
SOCI[4s3p1d]	4.790	325	252
SOCI+Q[4s3p1d]	4.796	324	439
FCI[4s3p1d]	4.790	325	289
SDCI[5s4p1d]	4.767	333	1132
CPF[5s4p1d]	4.777	324	828
SDCI[4s3p2d]	4.753	331	1007
CPF[4s3p2d]	4.760	327	692
MRCI[4s3p2d]	51 ^a
MRCI+Q[4s3p2d]	367 ^a
SOCI[4s3p2d]	128 ^a
SOCI+Q[4s3p2d]	318 ^a
FCI[4s3p2d]	158 ^a
SDCI[5s4p2d]	4.742	330	1051
CPF[5s4p2d]	4.748	328	734
SOCI[5s4p2d]	4.746	336	160
SOCI+Q[5s4p2d]	4.749	334	375
SDCI BIG-GTO	4.701	343	1072
CPF BIG-GTO	4.702	342	742
SDCI BIG-GTO(22)	4.675	344	1524
CPF BIG-GTO(22)	4.679	341	716
SDCI STO	4.699	344	1114
CPF STO	4.700	343	742
SDCI BIG-ANO	4.709	344	1105
CPF BIG-ANO	4.711	342	780
MRCI BIG-ANO	4.705	345	77
MRCI+Q BIG-ANO	4.710	343	419
SOCI BIG-ANO	4.710	344	165
SOCI+Q BIG-ANO	4.711	343	383
SOCI+Rel ^b BIG-ANO	4.710	343	174
EXPT	4.660	350	

^a The bond length is 4.750; based upon the SDCI and CPF calculations this results in about a 2 cm⁻¹ uncertainty the T_e.

^b Indicates that an estimate of relativistic effects was included.

Table V. Comparison of Al_2 $a^1\Sigma_g^+$ spectroscopic constants with level of basis set and correlation treatment.

	r_e (a_0)	ω_e (cm^{-1})	T_e (cm^{-1})
SDCI[4s3p1d]	5.747	223	3155
CPF[4s3p1d]	5.741	210	2682
FCI[4s3p1d]	5.739	202	2685
SDCI[5s4p1d]	5.730	223	3115
CPF[5s4p1d]	5.726	210	2652
SOCI[5s4p2d]	5.718	205	2832
SOCI+Q[5s4p2d]	5.692	192	3033
SDCI BIG-GTO	5.615	230	2856
CPF BIG-GTO	5.583	216	2326
SDCI BIG-GTO(22)	5.566	240	3425
CPF BIG-GTO(22)	5.581	216	2463
SDCI STO	5.593	237	2800
CPF STO	5.557	225	2281

Table VI. SOCI+Q Franck-Condon factors for the $(1)^3\Pi_u-(2)^3\Pi_g$ transition using the [5s4p2d] ANO basis.

transition	$q_{0,v'}$	energy(cm^{-1})	$\Delta(\text{cm}^{-1})$
0 \rightarrow 0	0.00363	23 387	...
0 \rightarrow 1	0.13711	23 755	367
0 \rightarrow 2	0.67005	23 966	212
0 \rightarrow 3	0.13855	24 120	154
0 \rightarrow 4	0.04341	24 257	136
0 \rightarrow 5	0.00047	24 392	135